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# Characterization of carbon monoxide, methane and nonmethane hydrocarbons in emerging cities of Saudi Arabia and Pakistan and in Singapore

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**Abstract** We investigate the composition of 63 C<sub>2</sub>–C<sub>10</sub> nonmethane hydrocarbons (NMHCs), methane (CH<sub>4</sub>) and carbon monoxide (CO), in Jeddah, Mecca, and Madina (Saudi Arabia), in Lahore, (Pakistan), and in Singapore. We established a database with which to compare and contrast NMHCs in regions where ambient levels and emissions are poorly characterized, but where conditions are favorable to the formation of tropospheric ozone, and where measurements are essential for improving emission inventories and modeling. This dataset will also serve as a base for further analysis of air pollution in Western Saudi Arabia including, but not limited to, the estimation of urban emissions and long range pollution transport from these

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regions. The measured species showed enhanced levels in all Saudi Arabian cities compared to the local background but were generally much lower than in Lahore. In Madina, vehicle exhaust was the dominant NMHC source, as indicated by enhanced levels of combustion products and by the good correlation between NMHCs and CO, while in Jeddah and Mecca a combination of sources needs to be considered. Very high NMHC levels were measured in Lahore, and elevated levels of CH<sub>4</sub> in Lahore were attributed to natural gas. When we compared our results with 2010 emissions from the MACCity global inventory, we found discrepancies in the relative contribution of NMHCs between the measurements and the inventory. In all cities, alkenes (especially ethene and propene) dominated the hydroxyl radical (OH) reactivity ( $k_{\text{OH}}$ ) because of their great abundance and their relatively fast reaction rates with OH.

**Keywords** Nonmethane hydrocarbons · Tropospheric chemistry · Urban air · Tropospheric ozone · Emission inventories · Gas-chromatography

## 1 Introduction

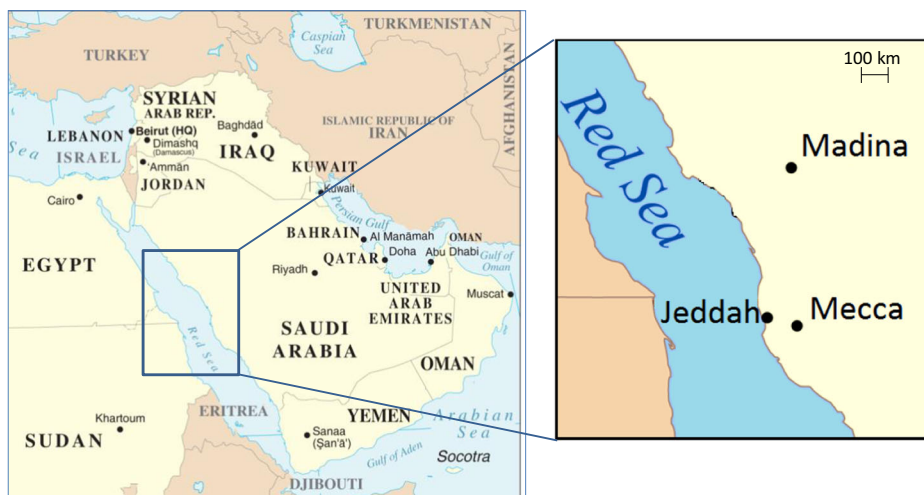
Nonmethane hydrocarbons (NMHCs) are an important component of volatile organic compounds (VOCs). In urban areas, when coupled with nitrogen oxides (NO<sub>x</sub>) in the presence of sunlight, they are key chemical precursors of tropospheric ozone (O<sub>3</sub>) (Poisson et al. 2000 and references therein) and other photochemical pollutants that negatively impact human health, such as aldehydes and peroxyacetyl nitrate (White 1994; Frampton et al. 1999; Sanhueza et al. 2003). Vehicular emissions (including gasoline distribution, evaporation and car exhaust), fuel production, industrial emissions, and solvent evaporation are among the most important NMHC sources in cities (Derwent 1995; Guo et al. 2007; Baker et al. 2008). In addition to these anthropogenic sources, natural sources can contribute to the overall levels of selected species, such as isoprene and the pinenes (Waked et al. 2012; McCarthy et al. 2013). The atmospheric abundance of NMHCs result from different factors, primarily the presence of local emission sources, their transport in and out of the area, and their loss by oxidation with atmospheric agents, mainly reaction with hydroxyl radicals (OH). To determine the relative importance of the different hydrocarbons toward O<sub>3</sub> production, a detailed speciation of NMHCs in urban areas is needed. For this reason, in the present study we characterize the composition of carbon monoxide (CO), methane (CH<sub>4</sub>), and NMHCs in the urban atmosphere of three cities in Saudi Arabia and we compare them with the tropospheric composition of two other Asian urban centers, namely Lahore (Pakistan) and Singapore. The relative amounts of NMHCs measured in this study are also compared to those provided by a standard global emissions inventory (MACCity). Emissions inventories used in global and regional chemistry models include very limited information about the speciation of VOCs (Lamarque et al. 2010); therefore, these observations provide critical information for improving them.

The NMHC composition of many urban areas has been extensively studied in the past decades, but the need for information is great, especially in rapidly growing urban areas in developing countries (e.g., Fenger 1999). Little is known about the air quality in Saudi Arabia (Lelieveld et al. 2009), much less about the overall NMHC composition and distribution in urban areas such as Mecca, Jeddah, and Madina, three of the most populated cities in Saudi Arabia. A companion study by Simpson et al. (2014) evaluated the impact of the 2012 Hajj (one of the largest religious pilgrimages in the world) on the air quality of Mecca, with samples

collected during the 2012 Hajj in urban areas of Mecca and along the pilgrimage route, with particular attention to the air composition inside the city tunnels used by both vehicles and pedestrians. Many NMHCs showed enhanced levels (particularly in the city tunnels) when compared to the regional background. The present study builds on this work by evaluating three urban areas in Saudi Arabia, and comparing them to measurements in Lahore and Singapore and to emissions from the MACCcity global inventory.

Mecca (21.42 °N, 39.82 °E; population of 2 million), the capital of Mecca Province (the most populous province of Saudi Arabia), is located about 70 km from the Red Sea. Jeddah (21.54 °N, 39.17 °E; population of 3.2 million) is the second largest city in Saudi Arabia after the capital Riyadh, and it is the largest sea port on the Red Sea. Madina (24.47 °N, 39.60 °E; population of 1.3 million) is the second most important holy city in Islam after Mecca and is about 150 km from the Red Sea. All three cities are in the western part of Saudi Arabia (Fig. 1), while most of the oil and gas deposits are in the eastern portion of the country. The sampling campaign took place between October 18 and November 13, 2012 and between April 8 and 12, 2013. The NMHC composition from the Saudi Arabian urban areas was compared to data gathered in Lahore (samples collected from December 29 and 31, 2012) and Singapore (August–October, 2012 sampling). This comparison has two main purposes: to characterize and compare the NMHC profiles in different Asian cities and to expand the NMHC data sets currently available for populated cities in Asia, in order to improve existing emission inventories.

The characterization and speciation of NMHCs in Lahore to our knowledge has not been published before, making the present study the first campaign carried out in this city. Lahore (31.55 °N; 74.34 °E) has a population of about 7 million, second in Pakistan to Karachi (13.2 million). The increasing population and volume of traffic in Lahore is a characteristic of many cities in developing countries and, as a result, vehicular emissions are a dominant air pollution source in Lahore (Ghauri et al. 2007; Mahboob and Makshoof 2010; Colbeck et al. 2011). Based on total (non-speciated) NMHC measurements in Lahore in 2003–2004, the major source of NMHCs was attributed to evaporative loss and leakage from vehicles and storage facilities (Ghauri et al. 2007). Similarly, a 1998 investigation of the NMHC composition of



**Fig. 1** Geographical location of the sampling sites in Saudi Arabia

Karachi found that leakage of liquefied petroleum gas was the main source of methane and short chain alkanes, while vehicular emissions were the main contributors of the remaining NMHCs (Barletta et al. 2002).

The Republic of Singapore (Singapore; 1.30 °N; 103.80 °E; population of 5 million) has a tropical climate and is the financial center of Southeast Asia. Singapore air experiences strong dilution during the northeast and southwest monsoon seasons, with two transient inter-monsoon periods. With various developed industries and a substantial effort aimed at “greening” the city state, NMHC data for Singapore are needed to characterize its unique mixture of industrial and vegetation emissions in a modern, densely populated urban environment. Studies on the NMHC composition in the urban area of Singapore are limited. In February 2012 samples were collected in Singapore for the development and validation of the analysis of selected VOCs (> C<sub>5</sub> hydrocarbons, aromatics, oxygenated NMHCs, and halogenated compounds) using thermal desorption gas chromatography mass spectrometry (Wong et al. 2013). However, in order to test this analytical method, samples were collected about 100 m from an expressway (~360 m from the nearest residential area) and the impact of vehicular combustion was predominant.

We recognize that our study only offers a snap-shots of the air quality of these urban centers at the time of sampling and does not address, for example, the effect of meteorology. However, our work establishes an initial baseline for these Asian urban areas with a focus on the relative importance of the different NMHCs in terms of OH reactivity, a proxy used to evaluate tropospheric O<sub>3</sub> formation in a region characterized by severe O<sub>3</sub> air pollution (Lelieveld et al. 2009) and lack of direct O<sub>3</sub> measurements. Moreover, ground-based measurements are essential for improving emission inventories that characterize surface emissions used in air quality modeling.

## 2 Sampling locations

Sixty-five ground-level air samples were collected from various locations in the residential urban areas of Mecca, Jeddah, and Madina (32, 17, and 16 samples, respectively). The sampling spots were open air locations where residents or visitors carry out their regular daily activities (eat, shop, etc.). Specifically, in Mecca, the sampling was carried out near Abdul Rahman Faqid School, in the Rusaifa residential district and in the Kudai residential district. In Jeddah, samples were collected in the following districts: Al Khalidiyah, Al’Mahjar, Aziziyah, Al Jamia’ah and in the old district. Lastly, samples were collected in Madina near Jamia Taiba University, in the Aziziyah district, in a residential area near King Abdul Aziz Road, and in a residential area near Airport Road. The canisters were filled over a 1-minute period throughout the day and night, but not at regular intervals.

In Mecca, the first round of air sampling occurred in 2012 (October 19–November 1) when between October 24 and 29 the Hajj, one of the largest religious pilgrimages in the world, took place (the impact of the Hajj on the city’s air quality is discussed in Simpson et al. 2014). In our study, to characterize the composition of the urban area of Mecca, we excluded samples collected around pilgrimage sites during the Hajj and only used samples collected in residential areas. Moreover, the 20 residential samples from October 2012 show comparable levels to the 12 samples from the second round of sampling in April 2013 outside the Hajj period (Supplementary Figure 1), and for this reason are included in the data set used to characterize Mecca’s NMHC composition.

In Jeddah and Madina, samples were collected in residential areas in October–November 2012 (6 in Jeddah, 10 in Madina) and in April 2013 (11 in Jeddah and 6 in Madina), throughout the daytime and at night, with no specific sampling schedule. Finally, during both sampling campaigns, an additional 20 samples were collected in religious locations outside Mecca and around the Grand Mosque of Mecca (samples from the key days of the 2012 Hajj event were excluded). These samples are included in the overall data set (85 samples) and used throughout the paper to give a broad picture of NMHC levels in western Saudi Arabia.

A total of 41 samples were collected on December 29–31, 2012 in six different locations throughout Lahore (in proximity of the Anarhali open air bazaar, near the Chauburji and the Chungii monument, in the Shahdara northern suburb of Lahore, near Bahria Town in Lahore, near Multon Road, and in the Kotlakhpat area). One-minute flask-based samples were collected at midnight, 6 a.m., 12 noon, 6 p.m. and 9 p.m. in open air locations away from direct point sources. In Singapore, 85 canisters were filled on the rooftop of a five story building at the National University of Singapore (67 m above sea level) approximately once or twice daily mostly between 9 a.m. and 7 p.m. during August 16 to November 1, 2012. About half of the sampling period fell in the southwest monsoon season (which occurs between June and September) characterized by northerly to northeasterly winds, and half in the inter-monsoon period when winds are more variable (<http://www.weather.gov.sg/climate-climate-of-singapore/>). At the time of sampling in Singapore, moderate winds were observed (<1 to 5 m/s).

The different sampling schedule in the different urban locations (i.e. strict sampling schedule in Lahore compared to sampling at irregular intervals in Saudi Arabia and Singapore) was adopted to accommodate the available organizational resources. The different sampling strategy adopted in Singapore, with samples collected on a rooftop, is discussed in section 4.2.

### 3 Sample analysis and emissions inventory description

During sampling, evacuated 2 l electropolished stainless steel canisters were individually filled by slightly opening a bellows valve, allowing about a 1 min collection of an air sample. The canisters were then sealed and shipped to our laboratory at the University of California, Irvine (UCI) where they were analyzed for CO, CH<sub>4</sub>, and 63 NMHCs. Carbon monoxide and CH<sub>4</sub> analyses were carried out using a gas chromatograph (GC, HP 5890) equipped with a flame ionization detector (FID) and a 3 mm molecular sieve column for CO and a 1/8" stainless steel 0.9 m column packed with 80/100 mesh Spherocarb for CH<sub>4</sub> (samples analyzed for CO were injected and then converted to CH<sub>4</sub> in a catalyst after the chromatographic separation). A complete description of the GC parameters and analytical methods for the VOC analysis are given elsewhere (Colman et al. 2001; Simpson et al. 2010). Briefly, after 217 cm<sup>3</sup> of sample is cryogenically pre-concentrated, the sample is vaporized with hot water and split into five different streams directed to a multi-column/detector GC system (all HP 6890). The system consists of three Hewlett-Packard 6890 GC units. The first GC is equipped with two different column combinations output to an electron capture detector (ECD) and an FID; the second GC is output to an FID; and the third GC is equipped with two different column combinations and output to a quadrupole mass spectrometer detector working in selected ion monitoring (SIM) mode, and an ECD.

The measurement precision, detection limits and accuracy vary by compound. The detection limit is 3 pptv for NMHCs (CH<sub>4</sub> and CO are always above its detection limit). The accuracy of our measurements is 1 % for CH<sub>4</sub>, 5–7 % for CO, and 5 % for the NMHCs

reported here. The measurement precision is 0.1 % for CH<sub>4</sub>, 2 % for CO, and 3 pptv to 3 % for most NMHCs.

The relative contribution of NMHCs found in our study are compared (below) to the VOC speciation used in a widely-used global emission inventory, MACCcity (Granier et al. 2011; [http://accent.aero.jussieu.fr/MACC\\_metadata.php](http://accent.aero.jussieu.fr/MACC_metadata.php)). Briefly, the MACCcity emission inventory is an extension of the emissions inventory used for the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP). The ACCMIP inventory was created to provide gridded emissions of reactive species and aerosols to be used in chemistry model simulations for the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment report (AR5). MACCcity emission inventories are based on the 1990 and 2000 ACCMIP emissions, and the 2005 and 2010 RCP8.5 (Representative Concentration Pathways) emissions of the main tropospheric gases for the 1990–2010 period with a spatial resolution of  $0.5 \times 0.5^\circ$ . While this grid size is larger than the cities sampled in this study, the relative contributions of hydrocarbons in the inventory is expected to be representative of the cities. The broad sampling performed in each city provides an overall characterization of each urban area that make the observations suitable for this evaluation of the NMHC speciation.

A quantification of the uncertainties associated with any emissions inventory is very difficult (e.g., Granier et al. 2011). The MACCcity inventory was compared to a number of other emission inventories for black carbon, CO, nitrogen oxides and sulfur dioxide and no substantial biases were found (Granier et al. 2011). Evaluations of NMHC emissions inventories have rarely been considered (e.g., Li et al. 2014). For this reason, it can be assumed that the 2010 MACCcity inventory has similar uncertainties (as large as a factor of 2) to those associated with other published emission estimates for which the uncertainties were provided (Amnuaylojaroen et al. 2014).

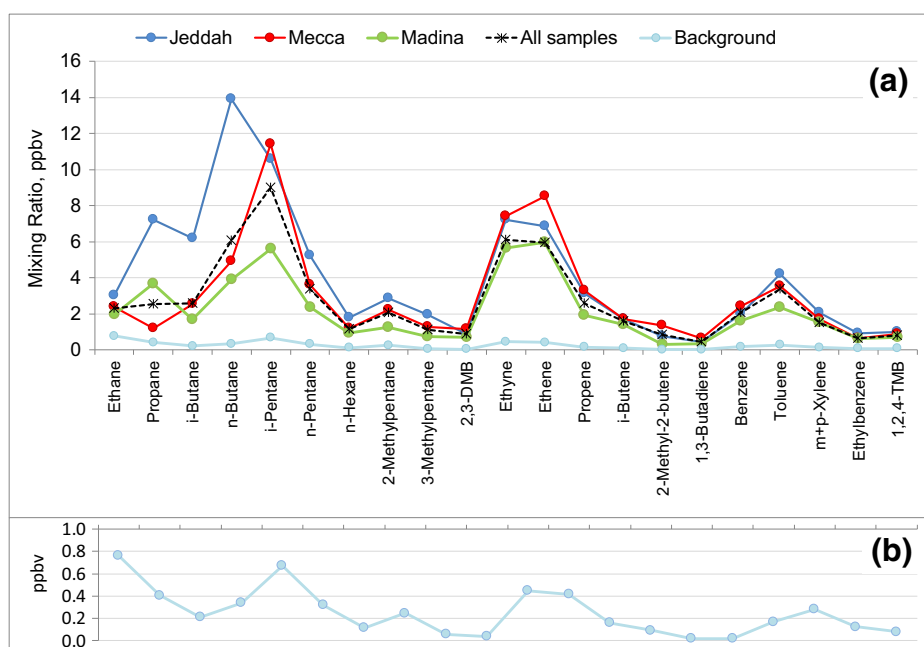
## 4 Results and discussion

### 4.1 General overview in Saudi Arabia

Mixing ratios were calculated for CO, CH<sub>4</sub>, and 63 different NMHCs, including 28 alkanes, 20 alkenes, ethyne, and 15 aromatic compounds (halogenated compounds were also quantified, but are not included in this study). The range of NMHC levels measured in the different cities varied greatly. For instance, *i*-pentane, the most abundant NMHC measured in the entire Saudi data set (85 samples), ranged over more than four orders of magnitude, from a minimum of 0.16 ppbv in Jeddah, which can be considered a relatively low level for an urban area, to a maximum of 734 ppbv in the Shisha district (at the border of Mecca and Mina) in April, 2013 (3 p.m. sample). Even when care is taken not to sample in the vicinity of direct point sources (i.e. car tailpipe, industrial areas, and storage of fuel such as LPG or gasoline), this high variability is not unusual in urban areas where strong NMHC emission sources co-exist with low background levels. To reduce the weight of these highly concentrated samples, we use the median values to represent the overall levels. The uncertainty associated with the median value is evaluated using the standard error of the median (SE<sub>med</sub>). The statistics for the trace gases measured in Jeddah, Mecca, and Madina are presented in Supplementary Tables 1–3.

The 20 most abundant NMHCs in the entire Saudi Arabia data set are ten alkanes (C<sub>2</sub>–C<sub>6</sub>), followed by four alkenes (C<sub>2</sub>–C<sub>5</sub>), five aromatics (C<sub>6</sub>–C<sub>8</sub>) and ethyne (Fig. 2). To put the median levels measured in Saudi Arabia into perspective, Fig. 2 also shows the median mixing





**Fig. 2** **a** Median mixing ratios (ppbv) calculated for the 20 most abundant NMHCs measured in Jeddah, Mecca, Madina, and in the 85 total samples collected in Saudi Arabia (“all samples”). 1,3-Butadiene has been included given its adverse health effects. **b** As (a) showing detail for the local background mixing ratios. DMB = dimethylbutane; TMB = trimethylbenzene

ratio calculated for the lowest 10th percentile of the entire data set (about 9 samples). This value can be considered a useful indicator of the “regional background” and suggests the lowest value NMHCs can attain in the vicinity of the urban locations investigated here. Supplementary Tables 1–3 and Fig. 2 show that all the measured species were highly enhanced in the Saudi Arabian cities compared to the local background samples. Overall, the highest load of NMHCs (by volume) was observed in Jeddah ( $99.6 \pm 9.6$  ppbv), followed by Mecca ( $79.5 \pm 8.4$  ppbv) and Madina ( $52.8 \pm 10.6$  ppbv). The NMHC load for the regional background was 9 to 16 times lower, at  $6.1 \pm 0.21$  ppbv.  $C_2$ – $C_4$  alkanes, pentanes, ethyne, ethene, propene, and toluene ranked among the 10 most abundant hydrocarbons in both Jeddah and Madina. The list is similar for Mecca, with the exception of propane which had lower levels (17th most abundant gas) compared to Jeddah and Madina. Figure 2 also highlights high levels of propane and the butanes in Jeddah.

In many urban areas a diurnal pattern in NMHCs can be observed, in many cases showing higher levels at night compared to daytime (Li and Wang 2012; Tu et al. 2007 and references therein). At night, the higher levels are the result of a shallow boundary layer and stable atmospheric conditions, and weaker sinks. After sunrise, changes in meteorological conditions (i.e. more unstable air, deeper boundary layer) and enhanced photochemical reactions lower the overall mixing ratios. Even though our sampling size is quite limited, we compared the mixing ratios of the samples collected during the daytime and nighttime for the Saudi Arabian cities (Table 1). Samples collected between 10 a.m. (the first sample collected after sunrise) and 7 p.m. are used for the daytime analysis and samples collected between 8 p.m. and 2 a.m. (last sample taken before sunrise) are used for the nighttime analysis. In Madina enhanced



**Table 1** Median mixing ratios (ppbv) measured during the daytime (10 a.m. to 7 p.m.) and nighttime (8 p.m. to 2 a.m.) in Jeddah, Mecca, and Madina for CO, CH<sub>4</sub>, 1,3-butadiene and the 20 most abundant species

|                    | Jeddah          |                |               | Mecca          |                 |               | Madina                 |                 |               |
|--------------------|-----------------|----------------|---------------|----------------|-----------------|---------------|------------------------|-----------------|---------------|
|                    | Day<br>N = 10   | Night<br>N = 7 | Day/<br>night | Day<br>N = 21  | Night<br>N = 11 | Day/<br>night | Day<br>(ppbv)<br>N = 8 | Night<br>N = 8  | Day/<br>night |
| CO                 | 0.8 (0.5)       | 1.2 (0.6)      | 0.6           | 1.5 (0.6)      | 1.6 (0.5)       | 0.9           | 0.8 (0.4)              | 1.6 (1.3)       | 0.5           |
| CH <sub>4</sub>    | 1860 (11)       | 1925 (24)      | 1.0           | 1868 (10)      | 1869 (28)       | 1.0           | 1859 (10)              | 1896 (40)       | 1.0           |
| Ethane             | 2.8 (0.6)       | 3.0 (0.5)      | 0.9           | 2.0 (0.4)      | 2.5 (0.9)       | 0.8           | 1.6 (0.6)              | 3.1 (1.0)       | 0.5           |
| Ethene             | 6.1 (2.8)       | 8.1 (3.4)      | 0.8           | 8.2 (2.7)      | 9.6 (2.8)       | 0.9           | 4.0 (1.4)              | 10.9 (6.1)      | 0.4           |
| Ethyne             | 6.2 (3.3)       | 9.8 (13.2)     | 0.6           | 6.1 (5.4)      | 10.5 (5.0)      | 0.6           | 4.3 (2.7)              | 11.9 (8.4)      | 0.4           |
| Propane            | 6.3 (2.5)       | 11.1 (4.4)     | 0.6           | 1.1 (0.5)      | 2.3 (1.6)       | 0.5           | 2.3 (0.6)              | 9.9 (4.2)       | 0.2           |
| Propene            | 2.8 (1.2)       | 5.0 (1.3)      | 0.6           | 3.0 (0.9)      | 4.6 (1.2)       | 0.7           | 1.3 (0.4)              | 4.0 (2.3)       | 0.3           |
| <i>i</i> -Butane   | 7.3 (1.9)       | 4.2 (2.1)      | 1.7           | 2.5 (1.3)      | 3.5 (1.3)       | 0.7           | 1.4 (0.2)              | 6.4 (2.5)       | 0.2           |
| <i>n</i> -Butane   | 20.8 (6.0)      | 9.4 (4.1)      | 2.2           | 4.8 (2.9)      | 6.4 (2.4)       | 0.7           | 3.5 (0.8)              | 15.3 (5.4)      | 0.2           |
| <i>i</i> -Butene   | 1.5 (1.0)       | 2.2 (0.7)      | 0.7           | 1.7 (0.7)      | 1.9 (0.7)       | 0.9           | 0.7 (0.3)              | 1.9 (1.8)       | 0.4           |
| <i>i</i> -Pentane  | 14.4 (6.1)      | 6.5 (3.5)      | 2.2           | 11.5 (8.6)     | 9.0 (4.6)       | 1.3           | 4.7 (1.5)              | 19.9 (9.3)      | 0.2           |
| <i>n</i> -Pentane  | 11.1 (4.6)      | 2.9 (1.3)      | 3.9           | 4.2 (2.4)      | 3.4 (1.3)       | 1.2           | 1.7 (0.6)              | 8.7 (3.7)       | 0.2           |
| 1,3-Butadiene      | 0.4 (0.1)       | 0.5 (0.2)      | 0.8           | 0.6 (0.2)      | 0.6 (0.2)       | 1.2           | 0.2 (0.1)              | 0.6 (0.3)       | 0.4           |
| 2-Methyl-2-butene  | 0.9 (0.8)       | 0.8 (0.5)      | 1.2           | 1.4 (1.4)      | 1.3 (0.5)       | 1.0           | 0.1 (0.2)              | 0.6 (0.3)       | 0.2           |
| <i>n</i> -Hexane   | 2.8 (1.5)       | 1.1 (0.4)      | 2.4           | 1.1 (0.7)      | 1.3 (0.4)       | 0.9           | 0.8 (0.2)              | 3.3 (1.6)       | 0.2           |
| 2,3-Dimethylbutane | 1.0 (0.6)       | 0.7 (0.4)      | 1.3           | 1.0 (0.7)      | 1.3 (0.4)       | 0.8           | 0.6 (0.1)              | 3.6 (2.6)       | 0.2           |
| 2-Methylpentane    | 3.8 (1.1)       | 1.9 (0.7)      | 2.0           | 2.1 (1.2)      | 2.3 (0.6)       | 0.9           | 1.1 (0.3)              | 4.4 (2.0)       | 0.3           |
| 3-Methylpentane    | 2.7 (0.7)       | 1.0 (0.4)      | 2.7           | 1.3 (0.7)      | 1.3 (0.4)       | 1.0           | 0.6 (0.1)              | 2.9 (1.5)       | 0.2           |
| Benzene            | 1.7 (0.6)       | 2.3 (0.6)      | 0.7           | 2.3 (0.9)      | 3.2 (0.7)       | 0.7           | 1.5 (0.9)              | 3.7 (2.4)       | 0.4           |
| Toluene            | 3.4 (1.2)       | 4.5 (1.5)      | 0.7           | 3.2 (1.8)      | 5.8 (1.5)       | 0.6           | 2.0 (0.4)              | 7.2 (3.6)       | 0.3           |
| 1,2,4-TMB          | 1.0 (0.5)       | 1.1 (0.5)      | 0.9           | 0.8 (0.8)      | 1.3 (0.6)       | 0.6           | 0.6 (0.1)              | 2.2 (1.7)       | 0.3           |
| Ethylbenzene       | 0.3 (0.1)       | 0.2 (0.1)      | 1.1           | 0.2 (0.1)      | 0.3 (0.1)       | 0.6           | 0.1 (0.03)             | 0.6 (0.4)       | 0.2           |
| <i>m+p</i> -Xylene | 1.8 (0.7)       | 2.3 (0.9)      | 0.8           | 1.4 (1.2)      | 2.8 (0.9)       | 0.5           | 1.2 (0.3)              | 4.8 (3.1)       | 0.2           |
| total NMHCs        | 135.3<br>(34.4) | 95.6<br>(36.9) | 1.4           | 85.3<br>(39.9) | 110.8<br>(28.7) | 0.8           | 47.1 (11.1)            | 152.4<br>(75.4) | 0.3           |

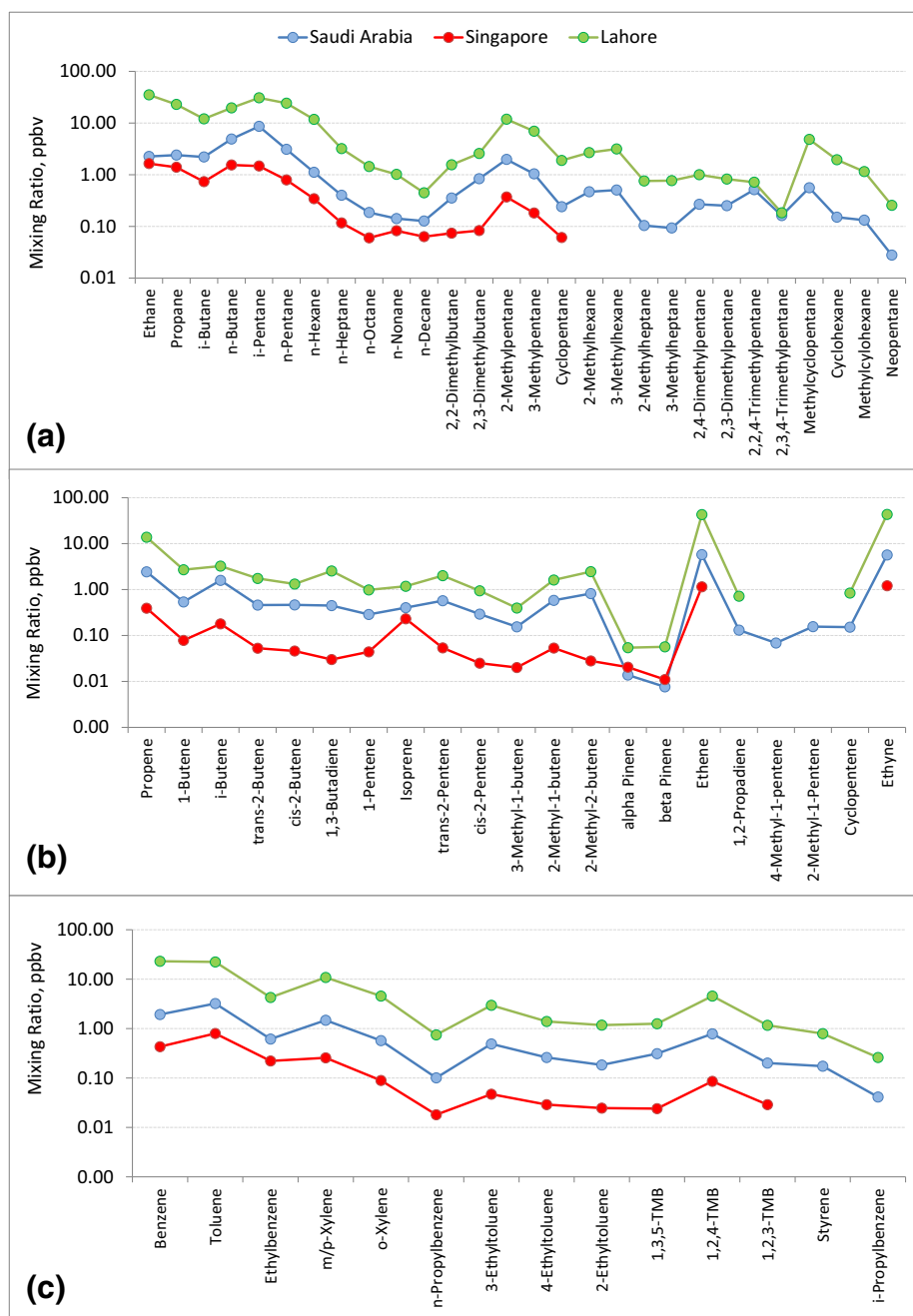
The uncertainty in the median value is reported in parenthesis

TMB trimethylbenzene, N number of samples

levels were observed at night compared to daytime. In particular, among the most abundant NMHCs and given the reported uncertainties, the median mixing ratio of alkanes (with the exception of ethane), 2-methyl-2-butene, toluene and *m+p*-xylene were higher at night compared to daytime. In Mecca, given the reported uncertainties, we cannot distinguish a clear diurnal pattern. In Jeddah, the majority of NMHCs are also not significantly different between day/night, but, among the 20 most abundant species, the median mixing ratios of *n*-butane, *n*-pentane, 2-methylpentane, and 3-methylpentane were higher during the daytime suggesting the presence of significant source of these species during this period.

## 4.2 Comparison among Saudi Arabia, Lahore, and Singapore

Atmospheric levels measured in Saudi Arabia were compared to those measured in Lahore, Pakistan and Singapore (Fig. 3; see Supplementary Tables 4 and 5 for statistics on Lahore and

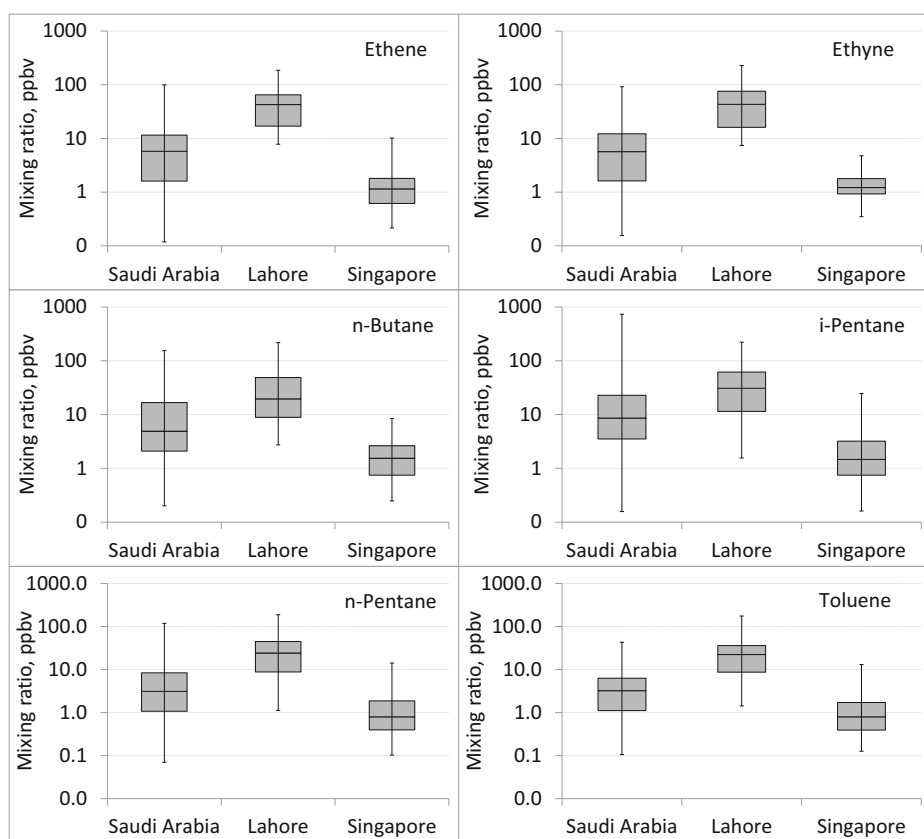


**Fig. 3** Median atmospheric mixing ratios (logarithmic plot) measured in Lahore, Singapore and Saudi Arabia (entire data set) for **a** alkanes, **b** ethyne and alkenes, and **c** aromatic species (TMB = trimethylbenzene). The uncertainties associated with these data can be found in Supplementary Tables 1–5. We note that because of the different sampling strategy in Singapore (see text for details), the data set collected in this city could be biased toward lower values

Singapore). These urban areas were investigated within 2 months of the first sampling campaign in Saudi Arabia in October 2012. For this comparison, we need to bear in mind the limitations posed by our “snap-shot” sampling, which, for example cannot be used to evaluate seasonal variations. Seasonality may be particularly important for Singapore because of the distinct monsoon seasons characteristic of this region. A study carried out over the Bay of Bengal (Sahu et al. 2011) found generally enhanced levels of NMHCs during the winter monsoon season compared to the summer monsoon season caused by the transport of anthropogenic emissions from the Asian continent during a time of prevailing northeasterly winds. Likewise, studies of air quality in Hong Kong show the impact of Asian monsoons, which bring more polluted air from Asia in winter and cleaner air from the South China Sea in summer (e.g. Guo et al. 2007). The conclusions from the Bay of Bengal and Hong Kong studies cannot be directly applied to Singapore because of its different geographical location. For these reason, even though we expect that the local meteorology affects the NMHC levels over Singapore, we cannot estimate its impact. Additionally, we note that the sampling in Singapore was carried out at the rooftop of a five story building, while in the other cities canisters were filled at about 2 m above the ground. For urban environments like Singapore with many high rise buildings, the topography in microscale is complicated. The dynamic urban flow as well as mixing is an on-going research. For these reasons, the rooftop sampling was chosen to represent the composition of the airborne pollutants relative to other (lower) locations. However, because of different atmospheric mixing properties, the data set collected in Singapore could be biased toward lower values and is most likely impacted by a more extensive footprint than at the surface. During this study we were unable to evaluate the impact of a different sampling height in Singapore and for this reason we need to bear in mind the difference in sampling strategy, particularly when absolute mixing ratios are compared among the different urban areas.

Similar to the data set collected in Saudi Arabia, we observe a high variability in the ambient mixing ratios measured in Lahore and Singapore, which is characteristic of urban environments where emission sources, transport/mixing, boundary layer fluctuations and diurnal variability in photochemistry all contribute to the observed NMHC levels. Despite this high variability, levels in Lahore stand out, and the median mixing ratio is higher in Lahore for almost all the measured species while the lowest levels were observed in Singapore. For instance, Fig. 4 shows box whisker plots for ethene, ethyne, *n*-butane, the pentanes, and toluene. For these species, the median mixing ratio in Lahore was 3–37 times higher than in both Singapore and Saudi Arabia and higher than the maximum mixing ratio measured in Singapore. Even though we observe a wide spread between the minimum and maximum mixing ratio measured in these locations, the minimum, maximum, lowest and top quartiles were all highest in Lahore, with the exception of the maximum *i*-pentane mixing ratio: 734 ppbv in Saudi Arabia versus 222 ppbv in Lahore.

The comparison between Lahore and Singapore reveals remarkable differences in the aromatic fraction and in selected alkenes. In Lahore, the aromatic species were enhanced by 20–60 times compared to the median levels measured in Singapore. In light of the possibility that levels in Singapore were biased toward lower values because of the different sampling strategy, we repeated this comparison using the value of the top quartile (Q3) to represent the aromatic fraction in Singapore (see Q3 in Supplementary Table 5). The aromatic component in Lahore is 7–37 times higher with respect to the top quartile of Singapore’s data set. Furthermore, with the exception of ethylbenzene, aromatics’ median values in the Pakistani city are still higher than the maximum mixing ratio measured in Singapore. Sources for aromatic



**Fig. 4** Box and whisker plots for ethene, ethyne, *n*-butane, *i*-pentane, *n*-pentane and toluene measured in Saudi Arabia, Lahore and Singapore. The *middle line* in the box represents the median value, the *top and bottom* of the box are the highest and lowest quartile, respectively, and the *error bar* represents the minimum and maximum measured mixing ratio

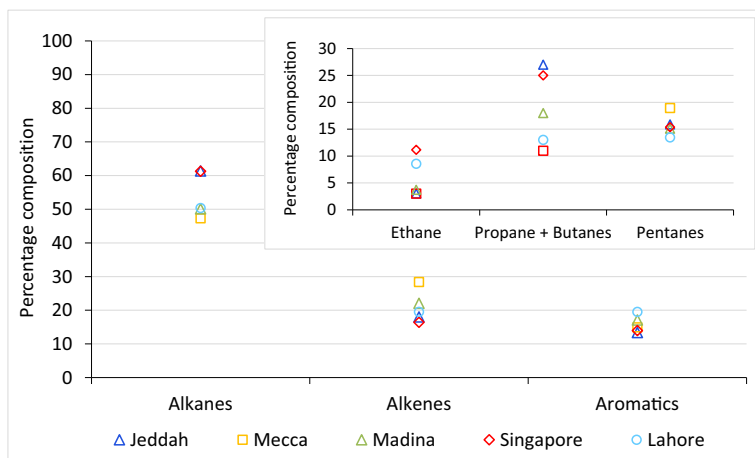
compounds in urban areas are mainly related to vehicular emissions and emissions from paints, industrial cleaners and solvents (Saxer et al. 2006; Park et al. 2010; Zheng et al. 2013). The median benzene mixing ratio measured in Lahore ( $23.1 \pm 6.0$  ppbv) was even higher than levels observed inside the Mecca tunnels during the 2012 Hajj (median of 7.7 ppbv) where traffic was jammed and the ventilation was operating at full capacity, though the maximum value in Lahore (136 ppbv) was lower than the tunnel maximum during Hajj (185 ppbv) (Simpson et al. 2014). To put the observed benzene values in perspective, the Reference Concentration (RfC) for benzene established by the U.S. Environmental Protection Agency (EPA) is 9 ppbv (US EPA 2015a). The RfC is a reference point for a lifetime exposure and indicates the possibility of increased adverse health effects above this limit. The concentration pattern of the aromatic species is similar among the different urban centers (Fig. 3c), suggesting the presence of similar emission sources. The median mixing ratio for 1,3-butadiene in Lahore ( $2.5 \pm 0.49$  ppbv) is particularly striking given that this species is a known human carcinogen (Delzell et al. 1996; Macaluso et al. 1996) and its median value exceeds the RfC for Chronic Inhalation Exposure of 0.9 ppbv (US EPA 2015b). Despite the differences observed in the absolute mixing ratios, both Figs. 2 and 3 reveal a similarity in the pattern

of many individual species among these different urban areas, suggesting that the NMHC composition is mainly driven by the same sources.

To assess the overall composition of the species measured in these five cities, we looked at the percentage composition of different classes of NMHCs (Fig. 5). The alkanes, alkenes, and aromatics fraction in Singapore (61, 16, and 14 %, respectively) is remarkably similar to Jeddah (61 % of alkanes, 18 % of alkenes, and 13 % of aromatics). In Lahore, where the absolute levels of NMHCs stand out, the composition is very similar to Madina (50 % alkanes for both cities, 20–22 % alkenes, 17–20 % of aromatics). However, looking into specific gases, 27 % of the total NMHCs in Jeddah were represented by propane and the butanes ( $27.3 \pm 4.8$  ppbv), compared to only 11 % in Mecca ( $8.6 \pm 2.4$  ppbv), 18 % in Madina ( $9.2 \pm 4.4$  ppbv), and 13 % in Lahore ( $54 \pm 32$  ppbv). In Singapore, despite the low mixing ratios of measured light alkanes (see Supplementary tables 1–5), their contribution to the total NMHCs was among the highest: 25 % represented by propane and the butanes and 11 % represented by ethane (9 % in Lahore and 3–4 % in the Saudi Arabian cities). The contribution from pentanes or other higher alkanes was overall homogeneous. Both the percentage composition and the analysis of the absolute mixing ratios suggest the presence of a strong source of short chain alkanes (propane and the butanes) in Jeddah compared to Mecca and Madina (see Section 4.5). In Singapore, even though some of the higher alkanes were not measured (decreasing the absolute value of the total NMHCs in this city), a source of  $C_2$ – $C_4$  alkanes is suggested by the NMHC composition.

### 4.3 Comparison to 28 US cities and Karachi

We also compare our data to CO,  $CH_4$  and speciated NMHCs measured in 28 US cities (Baker et al. 2008) and in Karachi, Pakistan (Barletta et al. 2002) which both reported their data as mean value  $\pm$  1-sigma standard deviation. Samples were collected throughout a broad time frame for the US cities (1999–2005) while the Karachi data were gathered in December 1998–January 1999. Although comparison with these earlier data sets is challenging because of possible changes in many important factors affecting emissions (such as legislation, car fleet, gasoline composition, etc.), the Baker et al. 28 US cities report has become a benchmark for



**Fig. 5** Percentage composition of alkanes, alkenes, aromatics, and ethyne calculated for the three cities in Saudi Arabia, in Singapore and Lahore. The insert shows a further analysis of the alkane fraction

NMHC characterization in western urban centers, while Karachi represents another large Pakistani urban center sampled by our same technique more than 10 years prior to the current data.

Methane mixing ratios in Jeddah, Mecca, and Madina ( $1869 \pm 11$  to  $1884 \pm 14$  ppbv), Singapore ( $1813 \pm 7.5$  ppbv) and US cities (mean of  $1760 \pm 10$  to  $2250 \pm 320$  ppbv) are overall comparable but substantially lower than in both Lahore and Karachi (median of  $4771 \pm 550$  and mean of  $6300 \pm 4700$  ppbv, respectively). Methane is the second most important greenhouse gas after carbon dioxide, and its global background concentration has increased by about 25 ppb from 1998 to 2010 (Kirschke et al. 2013). Therefore, the differences between the early and later studies are more than can be accounted for by methane's global growth. In cities, its main sources include gas and oil production, industrial emission, landfills and waste treatment, and natural gas leakage (Gioli et al. 2012). The methane levels in both Pakistani cities are among the highest our research group has ever observed in any urban area. For instance, in Europe, respective median levels of  $2525 \pm 24$  ppbv and  $1864 \pm 5$  ppbv were measured in Milan, Italy (2001 sampling, Meinardi et al. 2008) and Marseille, France (2004 sampling; unpublished data). In China, methane mean mixing ratios measured in 2001 in 43 different cities ranged between  $1889 \pm 19$  and  $2356 \pm 399$  ppbv (Barletta et al. 2005).

The median value for many NMHCs measured in the Saudi Arabian and Pakistani cities was higher than the mean mixing ratio reported for any of the 28 US cities. In particular, Lahore also stands out for its high levels of aromatics compared to all the other urban centers, Karachi included. The highest levels of benzene and toluene are observed in Lahore (median of  $23.1 \pm 6.0$  ppbv and  $22.3 \pm 7.5$  ppbv, respectively) followed by Karachi (mean of  $5.2 \pm 4.5$  and  $7.1 \pm 7.6$  ppbv, respectively), Saudi Arabia, US cities (mean of  $0.06 \pm 0.02$  to  $0.48 \pm 0.24$  ppbv for benzene and  $0.12 \pm 0.06$  to  $1.5 \pm 0.88$  ppbv for toluene), and lastly, Singapore where the maximum measured mixing ratio for benzene (3.6 ppbv) was lower than the mean level in Karachi and about 6 times lower than the median level measured in Lahore (toluene maximum mixing ratio in Singapore was 13 ppbv; Supplementary Table 5). Median levels of the two combustion tracers ethene and ethyne in Lahore ( $42.9 \pm 8.7$  ppbv and  $43.1 \pm 10.7$  ppbv, respectively) were highly elevated compared to those reported for Karachi (mean of  $19.0 \pm 17.0$  ppbv and  $18.0 \pm 16.2$  ppbv, respectively) and in Los Angeles (mean of  $2.4 \pm 1.5$  ppbv for both species), the US city with the highest levels. In Saudi Arabia these two combustion tracers were about twice as in Los Angeles. Major differences in the alkane mixing ratios were observed again between Lahore and the other urban areas, with the exception of the butanes which had similar levels in the Pakistani cities ( $11.0 \pm 9.1$  ppbv for *i*-butane and  $19.8 \pm 16.8$  ppbv for *n*-butane in Karachi). Mean levels of ethane and propane are approximately twice in Karachi compared to Lahore, while the opposite is observed for the pentanes.

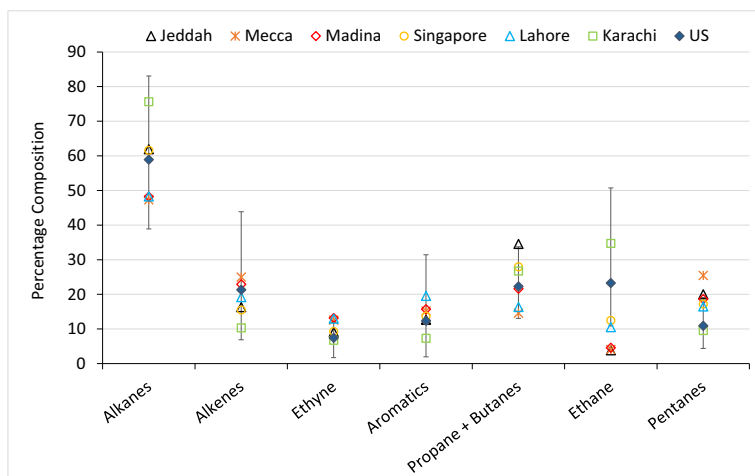
This comparison highlights that the hydrocarbon levels observed in Lahore are consistently higher than those observed in the other urban centers. Differences between the two Pakistani cities were smaller than differences between Lahore and the US cities, Saudi Arabian cities, and Singapore (where we need to bear in mind that a different sampling strategy was adopted). In the case of Karachi and Lahore, it is not possible to determine whether the higher concentrations in Lahore are related to increased concentrations with time or to pre-existing differences between Lahore and Karachi (a follow-up study in Karachi would help to clarify this).

Finally, we compare the percentage composition of selected NMHC measured in the US cities and Karachi to the findings from the Saudi Arabian cities, Lahore, and Singapore. For the purpose of this comparison, we only consider the species targeted in the 28 US cities study,

namely nine alkanes (ethane, propane, butanes, pentanes, hexane, heptane and octane), four alkenes (ethene, propene, 1-butene, and *i*-butene), ethyne, and five aromatics (benzene, toluene, ethylbenzene and the xylenes) and for this reason the percentage composition for the Saudi Arabian cities, Lahore and Singapore is slightly different than what reported in section 4.2. In Karachi, the alkane fraction dominates with 77 %, followed by alkenes (22 %), aromatics (11 %), and ethyne (7 %). A wide spectrum of composition is observed for the US urban areas: 39–83 % of alkanes, 7–44% of alkenes, 2–12 % of ethyne, and 2–31 % of aromatics. With such a wide range of composition, all the comparison cities (Karachi, Lahore, Singapore and the Saudi Arabian cities) fall within these values (Fig. 6). However, some unique features can be observed when the alkane fraction is further separated. The ethane composition in all the three Saudi Arabian cities is particularly low (4–5 %), lower than any of the 28 US cities (11–51 %), Singapore (12 %) or Lahore (10 %, consistent with the low end of the US values). The contribution from propane and butane to the NMHCs is particularly high in Jeddah (35 %), similar to the five urban centers in the US with the highest propane and butane contribution at 32–34 %. The pentanes are also particularly important in Jeddah (20 %), Mecca (25 %), and Madina (19 %) with a contribution similar or higher than in Las Vegas, the US cities with the highest pentanes fraction (19 %). Finally, the contribution from the combustion product ethyne to the total NMHCs is particularly high in Mecca, Madina, and Lahore (13 %) compare to Jeddah (9 %) the US cities (2–12 %), Singapore (9 %) or Karachi (7 %).

#### 4.4 Comparison to emissions inventory

We compare our results with the MACCity global emissions inventory for 2010 (Granier et al. 2011). The evaluation of emission inventories is critical as it improves the accuracy of air quality models and has been the focus in several studies where results obtained from observations (absolute or relative) were compared to emissions from both regional and global



**Fig. 6** Percentage composition of selected classes of NMHCs or individual species calculated for the different urban areas. The value reported for the US is the average of the values calculated for each of the 28 urban areas while the error bar for the US value represent the highest and lowest value calculated among the 28 urban areas. US data from Baker et al. 2008; Karachi data from Barletta et al. 2002; other data from present study



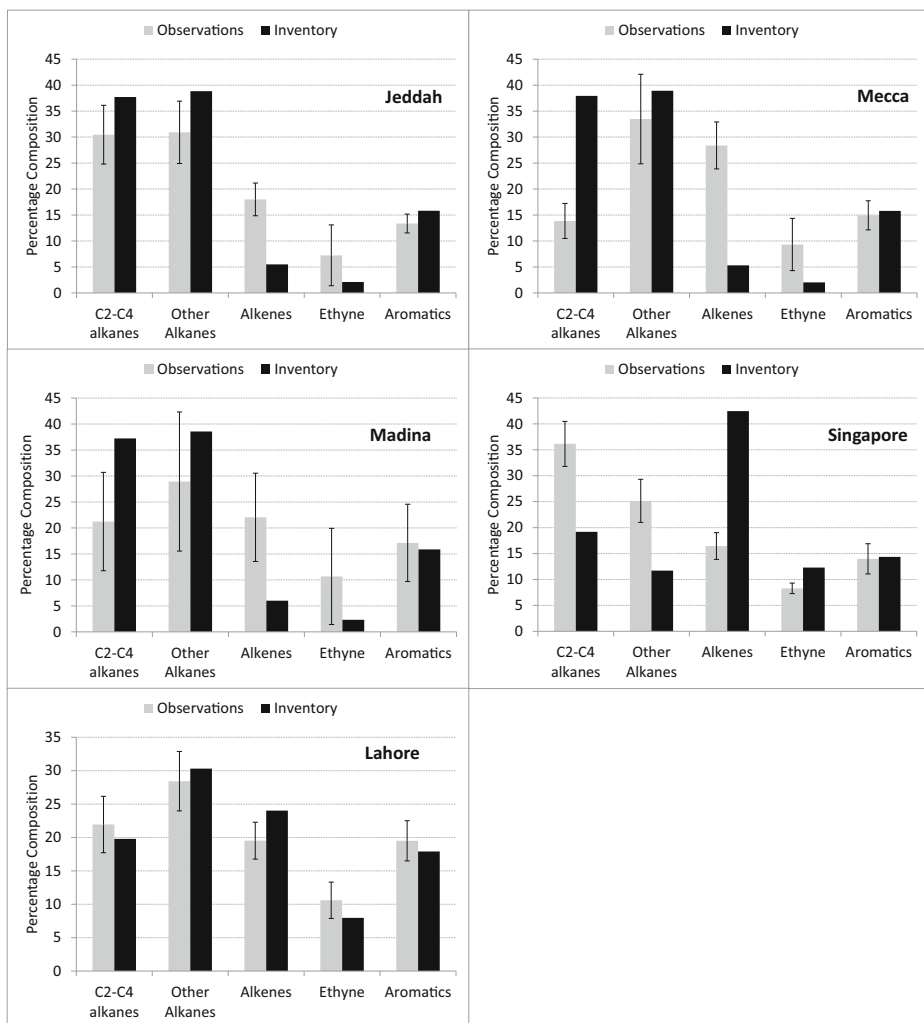
inventories. For instance, the annual NMHCs transportation emissions obtained from observations and positive matrix factorization (PMF) for Lebanon was compared to the estimates from the global historical emission inventory ACCMIP (Atmospheric Chemistry and Climate Model Intercomparison Project; Lamarque et al. 2010) and to the National Emission Inventory for Lebanon (Salameh et al. 2015). In both cases, emission inventories were found to be lower than observation-based emissions by a factor of 8–10. In Paris and Los Angeles, urban emission ratios relative to CO and ethyne were compared to emission ratios obtained from national and regional emission database in Los Angeles, and from the regional emission inventory in Paris. Large discrepancies up to a factor of four were observed, possibly caused by a bias in CO emissions in the inventories (Borbon et al. 2013).

While the observed mixing ratios cannot be directly compared to emission fluxes, the relative contribution of NMHCs at each of the observation site is compared to the NMHC speciation provided in the emission inventory. The speciation of VOCs in the MACCity inventory here used is the same as that in the historical emissions described by Lamarque et al. (2010). In our analysis we have compared the relative emission rates provided in the MACCity inventory for species that were also measured during our sampling campaign, namely CO, ethane, ethene, ethyne, propane, propene, butanes, pentanes, higher alkanes, higher alkenes, benzene, toluene, trimethylbenzenes, xylenes, and other aromatics. For the purpose of this comparison, we calculated the relative contribution of various classes of NMHCs (Fig. 7) or individual hydrocarbons (Supplementary Figure 2) to the sum of the species provided by both the MACCity inventory and the observations (total NMHCs). We then compare the “observed” NMHC speciation to the speciation of MACCity. Bearing in mind that our analysis neglects the possible effect that chemical transformation processes have on the observed NMHC mixing ratios, in the following we compare the fraction of each hydrocarbon, or class of NMHCs, to the total of all NMHCs that were observed.

In Saudi Arabia, the highly reactive alkenes and ethyne are underrepresented in the MACCity inventory (Fig. 7). Our observation is consistent with the results from Lebanon, where ethene emissions from the MACCity inventory were lower by a factor of six compared to the estimates obtained from observations and PMF (Salameh et al. 2015). By contrast to the alkenes, the observed alkane composition was higher than the inventory, driven by propane, the butanes, and the pentanes (Supplementary Figure 2). Benzene and toluene were overrepresented in the inventory, while the opposite was observed for other aromatics (including xylenes and trimethylbenzenes), resulting in an overall agreement for the aromatic fraction. In Singapore, a much higher alkene component was found in the inventory (42 %) compared to our measurements ( $16 \pm 3$  %), while alkanes were underestimated by almost a factor of two in the inventory. There was overall good agreement for the aromatic fraction, even though benzene represented about 7 % of the NMHCs in the MACCity inventory, about twice that observed in the measurements. Lastly, in Lahore measurements and inventory showed a good agreement for the different groups of NMHCs, more so when the uncertainty in the observations are considered. The discrepancy between the measured relative fraction and the relative fraction provided by the inventory was between <1 and 4 % for the alkanes, alkenes, ethyne and aromatic component.

#### 4.5 NMHC source evaluation

To identify the contribution of specific sources to the ambient levels of CO, CH<sub>4</sub> and NMHCs different approaches can be used. Positive matrix factorization and chemical mass balance are



**Fig. 7** Percentage composition of ethyne and different classes of NMHCs calculated for Jeddah, Mecca, Madina, Singapore, and Lahore for the samples collected in our study (“observations”) and for the same species included in the MACCcity emissions inventory

powerful receptor models used in source apportionment (i.e. Gaimoz et al. 2007; Guo et al. 2012; Yuan et al. 2012; Zheng et al. 2013); but the available sample size in our study is lower than the more than 100 samples required to provide reliable source attribution. However, a first insight on the major sources that impact the measured species can be obtained through correlation analysis between the different NMHCs and source “tracers” (i.e. Baker et al. 2008; de Gouw et al. 2009; Russo et al. 2010; Miller et al. 2012; Parrish et al. 2012). Here CO was used as a tracer for combustion sources and we focused our analysis to CH<sub>4</sub>, 1,3-butadiene and the twenty most abundant NMHCs. Table 2 lists the coefficient of determination ( $R^2$ ) and slopes calculated for the NMHC/CO linear correlation analysis for the Jeddah, Mecca, and Madina, which do not account for the possible effect of photochemistry. In fact, as shown in previous works (Borbon et al. 2013; Boynard et al. 2014), the distribution of

**Table 2** Slope ( $\pm$  standard error, SE) and coefficient of determination  $R^2$  for the linear correlation of methane, 1,3-butadiene and the twenty most abundant species measured in Saudi Arabia with CO (ppbv/ppbv for all  $\text{CH}_4$  versus CO; ppbv/ppbv for all the other gases)

|                    | Jeddah<br>Slope $\pm$ SE; $R^2$ | Mecca<br>Slope $\pm$ SE; $R^2$ | Madina<br>Slope $\pm$ SE; $R^2$ |
|--------------------|---------------------------------|--------------------------------|---------------------------------|
| Methane            | $0.022 \pm 0.012$ ; 0.21        | $0.023 \pm 0.007$ ; 0.30       | $0.027 \pm 0.004$ ; 0.79        |
| Ethane             | $0.7 \pm 0.3$ ; 0.30            | $1.1 \pm 0.2$ ; 0.51           | $0.7 \pm 0.1$ ; 0.89            |
| Propane            | $0.7 \pm 2.3$ ; 0.01            | $1.1 \pm 0.4$ ; 0.19           | $3.0 \pm 0.4$ ; 0.79            |
| <i>i</i> -Butane   | $1.8 \pm 1.3$ ; 0.13            | $1.8 \pm 0.6$ ; 0.25           | $1.8 \pm 0.3$ ; 0.78            |
| <i>n</i> -Butane   | $4.3 \pm 3.6$ ; 0.09            | $3.7 \pm 1.2$ ; 0.25           | $4.0 \pm 0.6$ ; 0.80            |
| <i>i</i> -Pentane  | $9.9 \pm 2.8$ ; 0.46            | $9.8 \pm 3.6$ ; 0.20           | $7.1 \pm 0.5$ ; 0.94            |
| <i>n</i> -Pentane  | $3.8 \pm 2.7$ ; 0.12            | $2.9 \pm 1.0$ ; 0.24           | $2.8 \pm 0.3$ ; 0.89            |
| <i>n</i> -Hexane   | $1.0 \pm 0.9$ ; 0.08            | $0.9 \pm 0.2$ ; 0.37           | $1.3 \pm 0.1$ ; 0.94            |
| 2,3-DMB            | $1.0 \pm 0.2$ ; 0.55            | $0.8 \pm 0.2$ ; 0.26           | $2.0 \pm 0.1$ ; 0.97            |
| 2-Methylpentane    | $1.6 \pm 0.6$ ; 0.37            | $1.6 \pm 0.4$ ; 0.32           | $1.5 \pm 0.1$ ; 0.91            |
| 3-Methylpentane    | $1.0 \pm 0.3$ ; 0.42            | $0.9 \pm 0.2$ ; 0.33           | $1.1 \pm 0.1$ ; 0.93            |
| Ethyne             | $7.1 \pm 0.6$ ; 0.92            | $6.7 \pm 1.0$ ; 0.61           | $6.2 \pm 0.4$ ; 0.96            |
| Ethene             | $5.7 \pm 0.8$ ; 0.78            | $5.4 \pm 0.4$ ; 0.84           | $4.6 \pm 0.2$ ; 0.98            |
| Propene            | $2.2 \pm 0.6$ ; 0.51            | $2.1 \pm 0.2$ ; 0.77           | $1.8 \pm 0.1$ ; 0.98            |
| <i>i</i> -Butene   | $1.5 \pm 0.4$ ; 0.49            | $1.1 \pm 0.2$ ; 0.48           | $1.3 \pm 0.05$ ; 0.99           |
| 2-Methyl-2-Butene  | $1.2 \pm 0.4$ ; 0.40            | $1.5 \pm 0.6$ ; 0.20           | $0.2 \pm 0.02$ ; 0.89           |
| 1,3-Butadiene      | $0.3 \pm 0.04$ ; 0.80           | $0.4 \pm 0.04$ ; 0.78          | $0.2 \pm 0.01$ ; 0.97           |
| Benzene            | $1.2 \pm 0.2$ ; 0.76            | $1.6 \pm 0.2$ ; 0.69           | $1.8 \pm 0.1$ ; 0.93            |
| Toluene            | $2.6 \pm 0.4$ ; 0.72            | $2.9 \pm 0.4$ ; 0.66           | $2.8 \pm 0.2$ ; 0.96            |
| <i>m+p</i> -Xylene | $1.5 \pm 0.2$ ; 0.73            | $1.4 \pm 0.2$ ; 0.62           | $2.4 \pm 0.1$ ; 0.98            |
| Ethylbenzene       | $0.4 \pm 0.1$ ; 0.45            | $0.5 \pm 0.1$ ; 0.57           | $0.6 \pm 0.04$ ; 0.94           |
| 1,2,4-TMB          | $0.9 \pm 0.1$ ; 0.74            | $0.8 \pm 0.1$ ; 0.56           | $1.3 \pm 0.1$ ; 0.98            |

DMB dimethylbutane, TMB 1,2,4-trimethylbenzene

points within a scatterplot can be affected by photochemistry influencing the NMHC/CO emission ratios (calculated as the slope of the linear regression of the different species with CO). A comparison between correlations computed using daytime and nighttime samples can help to assess the role of photochemistry and to identify emission sources. Such analysis, however, requires a larger sampling size than what we have available here (particularly when daytime and nighttime samples are separated). Moreover, this approach assumes that photochemistry plays a minor role at night, an assumption that needs to be first validated given the elevated values in nighttime or early morning OH reactivity reported in previous studies (Ren et al. 2003; Lou et al. 2010). For this reasons, we start focusing on the presence or lack of correlation with CO (i.e. on the  $R^2$  value). Two outliers (Supplementary Figure 3) were excluded for purposes of the correlation analysis in Madina, and one outlier was not used in both Jeddah and Mecca. In Madina, all the species showed a very good correlation with CO ( $R^2 > 0.78$ ; Table 2) suggesting the predominant role of combustion among the emission sources. We observed that mixing ratios of two samples collected in this city on November 2012 at around midnight were particularly elevated (CO of 7.7 and 7.4 ppbv). To evaluate the possibility that the good correlations observed in Madina were driven by these two data points, the correlation with CO was re-calculated excluding these two samples. A good correlation

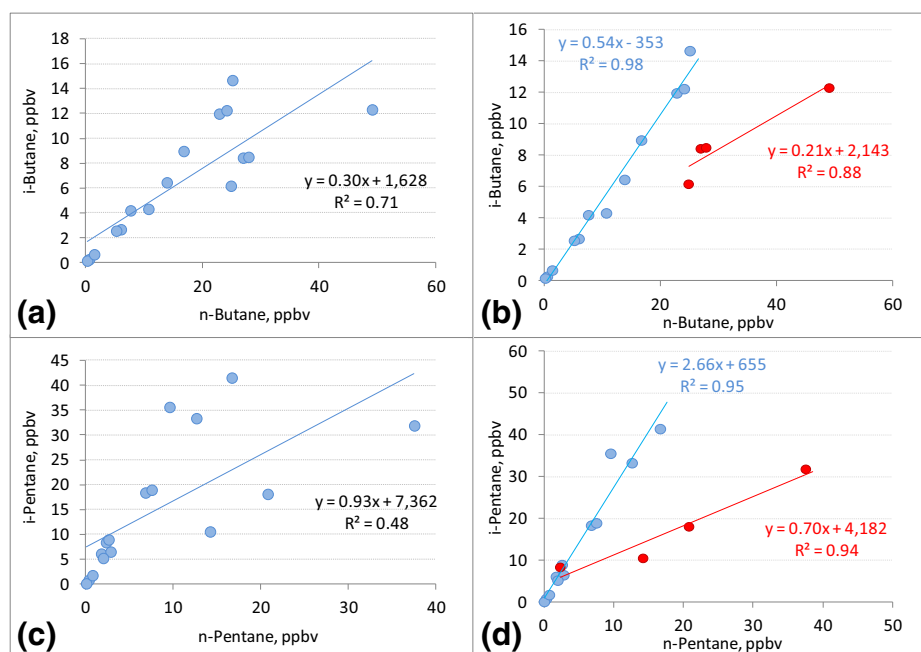
with CO was still observed with  $R^2 > 0.70$  for all the species, with the exception of methane. Methane  $R^2$  decreased from 0.79 to 0.64.

To differentiate between different combustion sources, we looked at the ambient ratios of species with similar lifetime. These ratios offer the advantage of being independent of dilution (as it affects both species equally) and, for compounds of similar reactivity toward OH, of oxidative removal (Russo et al. 2010). Ratios of propane vs ethyne, benzene vs ethyne, and propane vs benzene are typically  $< 1$  in vehicular exhaust and  $\geq 1$  in natural gas, LPG or gasoline vapor (Russo et al. 2010). In Madina, the benzene/ethyne correlation slope ( $0.29 \pm 0.01$  ppbv/ppbv,  $R^2 = 0.99$ ) and the propane/ethyne slope ( $0.50 \pm 0.05$  ppbv/ppbv,  $R^2 = 0.90$ ) indicate the influence of vehicular combustion among the possible combustion sources. The slope of propane vs benzene correlation ( $1.8 \pm 0.15$ ,  $R^2 = 0.92$ ) is higher than the ratio characteristic of vehicular combustion and, therefore, suggests the presence of another source of benzene in addition to vehicular combustion.

The source analysis was more complicated for Jeddah and Mecca. In both cities, a good correlation with CO ( $R^2 > 0.60$ ), suggesting the predominant influence of combustion sources, was observed for the aromatics (with the exception of ethylbenzene and 1,2,4-trimethylbenzene in Mecca), ethyne, ethene, and 1,3-butadiene; propene and CO also correlated well in Mecca (Table 2). All the alkanes and remaining alkenes correlated poorly with CO ( $R^2 \leq 0.55$ ) in both cities suggesting the presence of a different or additional source other than combustion for these species.

In Mecca, the butanes and all the  $\geq C_5$  compounds correlated well with each other ( $R^2$  0.76–0.97) with the *i*-pentane/*n*-pentane slope ( $3.6 \pm 0.13$ ,  $R^2 = 0.96$ ) consistent with both vehicular emissions (characteristic ratios of 2.2–3.8; Russo et al. 2010 and references therein) and fuel evaporation (ratios of  $\sim 3.8$ ; Russo et al. 2010 and references therein). The *i*-butane/*n*-butane slope ( $0.47 \pm 0.01$ ,  $R^2 = 0.97$ ) was higher than the urban/vehicular characteristic ratio of 0.2–0.3 and consistent with a ratio of 0.46 observed for LPG evaporation (Russo et al. 2010). These findings suggest that the butanes and  $\geq C_5$  species have a common source (or sources) other than (or in addition to) combustion. This additional influence is most likely resulting from LPG or other fuel evaporation.

In Jeddah, good cross-correlations between  $> C_5$  gases were observed with the exception of *i*-pentane, *n*-pentane, and *n*-hexane. The butane and pentane correlation plots show a bimodal distribution, with one trend generated by the majority of the data points and a second trend involving the same four individual samples (Fig. 8). Three of these samples were collected in the industrial district of Al-Mahjar, in proximity to one of the oldest refineries and the port area of Jeddah. The fourth data point corresponds to a sample collected in the residential district of Azizia, where apartment buildings are located close to an LPG sale point. While the sampling effort attempts to avoid direct point source, when sources have a heavy presence within an urban areas we are bound to pick up that source, and it is reflective of the urban environment. Here it seems likely that local activities related with the refinery, port operations, and LPG cylinder exchange affected the NMHC profile observed in these samples. When the four data points are removed, the pentanes and all the  $\geq C_5$  species show very good cross correlation ( $R^2$  0.90–0.98), suggesting a common source in Jeddah for these gases. In general, source (or sources) of propane, *i*-butane and *n*-butane appear to be particularly strong in Jeddah where median mixing ratios of  $7.2 \pm 2.4$ ,  $6.2 \pm 1.4$  and  $14 \pm 3.9$  ppbv, respectively were measured (Fig. 2 and Supplementary Table 1). *n*-Butane shows an excellent correlation with *i*-butane (Fig. 8b;  $R^2 = 0.98$  for the main trend line), a good correlation with *n*-hexane ( $R^2 = 0.71$ ), and a lack of correlation with propane ( $R^2 = 0.58$ ), and methane ( $R^2 = 0.50$ ). Because LPG is mainly a blend of propane, *i*-butane and *n*-butane, high



**Fig. 8** **a, b** *i*-Butane versus *n*-butane and **c, d** *i*-pentane versus *n*-pentane plots for the samples collected in Jeddah. Panels **a** and **c** show all the data points, the resulting linear equation, and  $R^2$ . Panels **b** and **d** show the two *trend lines* identified by separating out four data points

levels of these species in urban areas are commonly associated with LPG leakage. However, this appears not to be the case in Jeddah, where the good cross correlation among propane and the butanes expected from a LPG leakage source is lacking. Furthermore, the *i*-butane/*n*-butane slope ( $0.54 \pm 0.02$ ) is higher than the range of emission ratios reported for LPG evaporation, but also higher than the vehicular combustion ratio and lower than the ratio characteristic of natural gas (0.6 to >1; Russo et al. 2010). These findings highlight the need of further studies investigate the source (or sources) of these  $C_3$ – $C_4$  alkanes and  $\geq C_5$  species. In both Jeddah and Mecca ethylbenzene and 1,2,4-trimethylbenzene well correlate with toluene ( $R^2 = 0.78$ – $0.92$ ) suggesting a common source for these aromatic species.

Finally, we investigate the possible source (or sources) of the significantly enhanced levels of methane in Lahore. The good correlation of  $CH_4$  with ethane ( $R^2 = 0.67$ ) and lack of correlation with CO or any other NMHCs ( $R^2 < 0.05$ ) rules out combustion or LPG as the main methane source, and points instead to natural gas (NG). Furthermore, the absolute mixing ratios of methane and ethane are consistent with this hypothesis. In Lahore we observed an excess mixing ratio of 2938 ppbv for  $CH_4$  (assuming that the background of 1829 ppbv calculated using the Saudi Arabian data set is representative for Lahore as well) and of 34 ppbv for ethane (background of 0.70 ppbv). Natural gas composition varies by location, but methane is its main constituent (>90 %) followed by ethane, and a smaller fraction of propane and other alkanes. Assuming that all the excess methane measure in Lahore is released by NG leakage, the corresponding amount of ethane leaked by a NG composed of 97 % methane and 1 % ethane would be in the order of 30 ppbv, consistent with the 34 ppbv excess ethane measured in Lahore. Even though the exact composition of NG distributed in Lahore is not known, these findings all point to NG as the main source of methane in this urban area.

## 4.6 OH reactivity

The formation of tropospheric O<sub>3</sub> in urban areas is a complex process involving many different precursors. The key role of NMHCs in this process is well recognized and the oxidation process, ultimately leading to the formation of ozone, starts with the attack of an OH radical to a hydrocarbon. Therefore, the OH loss rate or “OH reactivity” ( $k_{\text{OH}}$ ; units of s<sup>-1</sup>) is a useful tool to quantify the load of reactive pollutants in an air mass and, bearing in mind the complexity of ozone formation, highly concentrated reactive species have a great potential to generate tropospheric ozone.

Relieveld et al. (2009) used a global atmospheric chemistry model to calculate tropospheric O<sub>3</sub> levels over the Persian/Arabia Gulf region. The annual minimum value was calculated to occur during the winter, while the annual daytime maximum during the summer often exceeded 80 ppbv. In addition to local photochemical processes, other factors contribute to the observed high level of ozone over the Middle East, particularly during the summertime in the mid to upper troposphere, such as long-range transport of polluted European air masses and downward transport of ozone from the upper troposphere and lower stratosphere associated with a large scale subsidence and limited horizontal divergence over this area (Zanis et al. 2014; Spohn and Rappengluck 2015). The Saudi Arabian ambient air quality limit for ozone in is set to 80 ppbv over a period of 8 h (PME 2013). Lower limits (over the same time period) are set worldwide. For instance, the 8-hour limit set by the European Union is 120 µg/m<sup>3</sup> (about 60 ppbv; <http://ec.europa.eu/environment/air/quality/standards.htm>) and the limit set by the US EPA is 75 ppbv (<http://www.epa.gov/air/criteria.html>).

In our study, in the absence of direct O<sub>3</sub> measurements, we calculate the OH reactivity to evaluate the importance of the different VOCs toward O<sub>3</sub> production. The main contributors to OH reactivity are VOCs, NO<sub>x</sub>, oxygenated VOCs (OVOCs), CO and to a lesser extent in urban areas, CH<sub>4</sub>. In our study, because of the lack of NO<sub>x</sub> and OVOC measurements, the calculated OH reactivity represents an underestimation of the real value. Using our data set, we calculated the  $k_{\text{OH total}}$  as:

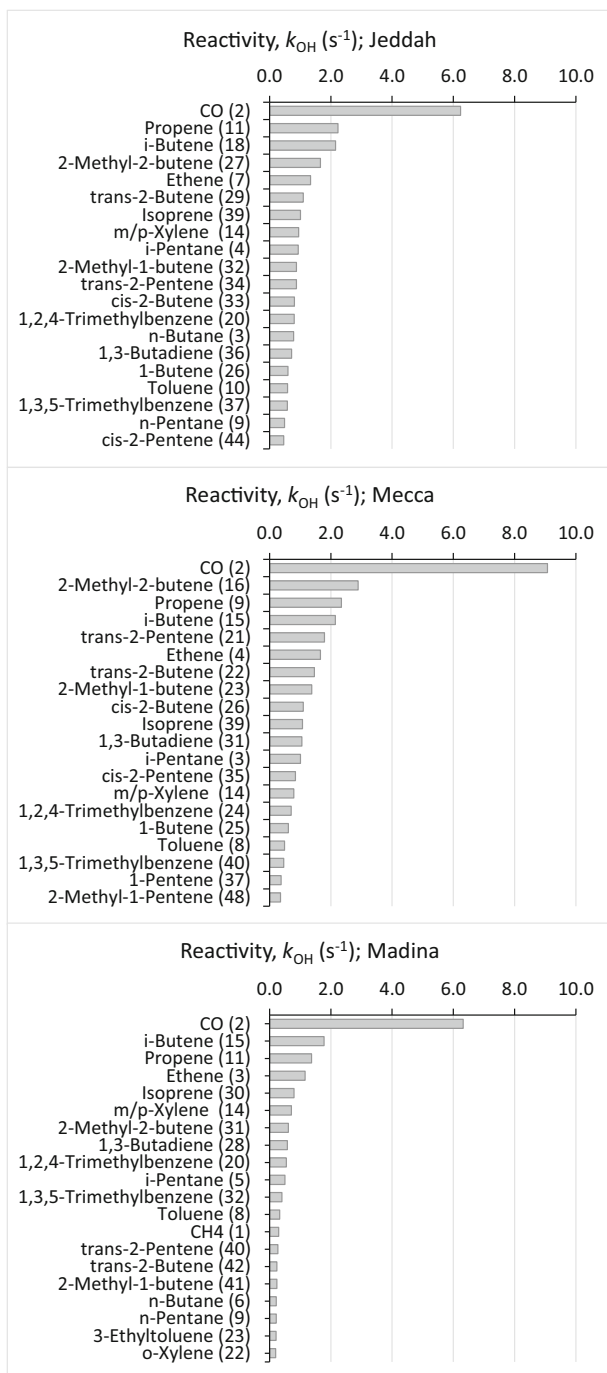
$$k_{\text{OH total}} = S k_{(\text{OH}+\text{NMHC}_i)}[\text{NMHC}_i] + k_{(\text{OH}+\text{CO})}[\text{CO}] + k_{(\text{OH}+\text{CH}_4)}[\text{CH}_4]$$

where  $k_{(\text{OH} + \text{NMHC}_i)}$  is the OH reaction rate constant coefficient for the specific NMHC<sub>*i*</sub> (Atkinson 2003; Atkinson et al. 2006; Atkinson and Arey 2007; <http://chem.sis.nlm.nih.gov/chemidplus/chemidlite.jsp>); [NMHC<sub>*i*</sub>] is the measured concentration of the specific gas listed in Supplementary Tables 1–3;  $k_{(\text{OH}+\text{CO})}$  and  $k_{(\text{OH}+\text{CH}_4)}$  are the rate constants for the OH reaction with CO and CH<sub>4</sub>, respectively; and [CO] and [CH<sub>4</sub>] are the concentrations of CO and CH<sub>4</sub>, respectively (units for  $k$ : cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; units for NMHCs, CO, and CH<sub>4</sub>: molecule cm<sup>-3</sup>).

The total reactivity for the measured NMHCs, CO, and CH<sub>4</sub> in Jeddah, Mecca, and Madina was 31 ± 3, 36 ± 4, and 20 ± 5 s<sup>-1</sup>, respectively. The NMHC contribution to the total reactivity ranged from 67 % in Madina to 79 % in Jeddah (74 % in Mecca), followed by CO (20 % in Jeddah, 25 % in Mecca, and 32 % in Madina) and CH<sub>4</sub> (0.8 to 1.5 %). In the background samples,  $k_{\text{OH}}$  (2.5 ± 0.1 s<sup>-1</sup>) was about 10× lower than the urban samples. In the background, the much lower contribution of NMHCs to the combined load of NMHCs, CO, and CH<sub>4</sub> reduced the NMHCs' contribution to  $k_{\text{OH}}$  to 48 %, with a 40 % contribution from CO (about double the urban samples) and 12 % from CH<sub>4</sub>.

Figure 9 illustrates the top 20 individual contributors in reactivity for the urban area of Jeddah, Mecca, and Madina. Carbon monoxide, alkenes and aromatics play the most important

**Fig. 9** Contribution to the OH reactivity,  $k_{OH}$ , for the top 20 contributors. The number in parenthesis after each species' name indicates the ranking in terms of median mixing ratio





role, while the alkanes are minor contributors (pentanes and *n*-butane for both Jeddah and Madina, *i*-pentane for Mecca). Only about half of the top 20 contributors to  $k_{\text{OH}}$  are also listed as top 20 species in atmospheric concentration. In particular, while CO is the second most abundant species in the three cities and also the top contributor to  $k_{\text{OH}}$ , methane, as the most abundant gas, is only ranked 24th, 23rd, and 13th in reactivity in Jeddah, Mecca, and Madina, respectively. Ethene, a top compound in terms of atmospheric concentration, is also an important contributor to  $k_{\text{OH}}$ .

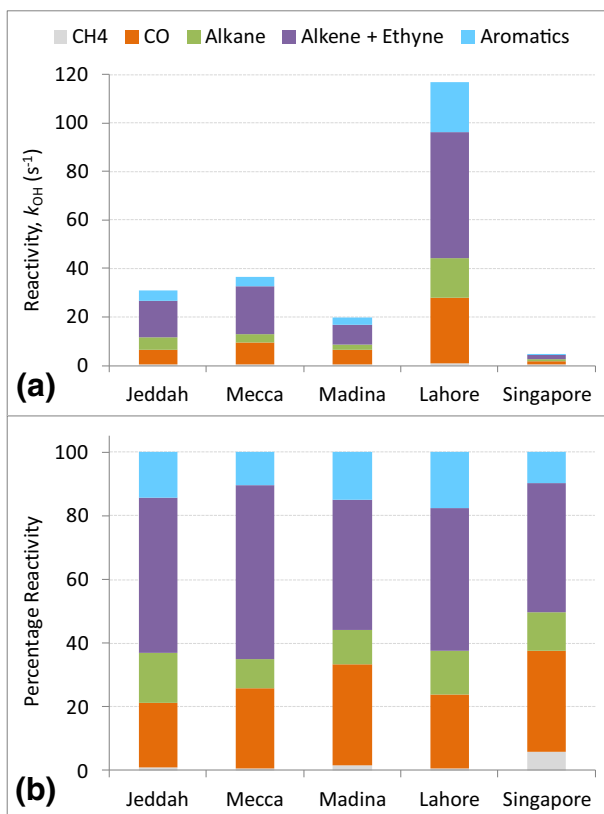
Given the overall higher NMHC levels observed in Madina during the nighttime (section 4.1), and the results from previous studies showing that  $k_{\text{OH}}$  can reach peak levels at night or during early morning (Ren et al. 2003; Lou et al. 2010), we calculated  $k_{\text{OH}}$  using daytime and nighttime samples (Table 3) for the Saudi Arabian cities. In Madina, the nighttime  $k_{\text{OH}}$  for the measured NMHCs was  $32 \pm 4 \text{ s}^{-1}$ , about three times higher than daytime and comparable to the nighttime reactivity calculated for Jeddah ( $26 \pm 3 \text{ s}^{-1}$ ) and Mecca ( $30 \pm 2 \text{ s}^{-1}$ ). All the NMHC classes, with the exception of the alkynes (i.e. ethyne), showed a higher  $k_{\text{OH}}$  at night; while no significant differences were observed between daytime and nighttime reactivity for CO and  $\text{CH}_4$ . Looking at individual NMHCs, the top contributors to  $k_{\text{OH}}$  in Madina are similar between daytime and nighttime, with CO, propene, *i*-butene, *m*+*p*-xylene, ethene, and *i*-pentane being the top five contributors for both time-periods. In Jeddah a higher daytime reactivity was observed for the alkane fraction ( $6.9 \pm 0.8 \text{ s}^{-1}$  versus  $3.5 \pm 0.5 \text{ s}^{-1}$  at night); while in Mecca a higher nighttime  $k_{\text{OH}}$  for the aromatic compounds ( $5.5 \pm 0.8 \text{ s}^{-1}$  versus  $3.2 \pm 1.0 \text{ s}^{-1}$  during the day) was calculated.

We also investigated differences in  $k_{\text{OH}}$  between the individual cities in Saudi Arabia, Lahore and Singapore (Fig. 10a) and compare to literature studies. Previous works report  $k_{\text{OH}}$  values ranging from 10 to  $100 \text{ s}^{-1}$  in cities such as Houston, Mexico City and Tokyo (Yoshino et al. 2006; Mao et al. 2009, 2010; Apel et al. 2010; Lou et al. 2010; Dolgorouky et al. 2012), with a maximum value of  $200 \text{ s}^{-1}$  reported in Mexico City (Shirley et al. 2006). These values, however, may include the contribution of inorganic compounds (such as  $\text{O}_3$ , CO,  $\text{NO}_x$ , etc.), and additional hydrocarbons (such as formaldehyde, OVOCs, and biogenics other than isoprene) while only CO,  $\text{CH}_4$ , and NMHCs are considered in our study. The OH reactivity derived for the Saudi Arabian cities falls within the range reported for other urban centers worldwide. Singapore and Lahore represent two opposite extremes, with a low reactivity

**Table 3** OH reactivity ( $k_{\text{OH}}$ ;  $\text{s}^{-1}$ ) calculated for the daytime (10 a.m. to 7 p.m.) and nighttime (8 p.m. to 2 a.m.) in Jeddah, Mecca, and Madina

|                            | Jeddah ( $k_{\text{OH}}$ ; $\text{s}^{-1}$ ) |                 | Mecca ( $k_{\text{OH}}$ ; $\text{s}^{-1}$ ) |                 | Madina ( $k_{\text{OH}}$ ; $\text{s}^{-1}$ ) |                 |
|----------------------------|--|-----------------|---|-----------------|--|-----------------|
|                            | Day  | Night           | Day   | Night           | Day  | Night           |
| CO + $\text{CH}_4$ + NMHCs | $30 \pm 4$                                   | $34 \pm 5$      | $35 \pm 6$                                  | $40 \pm 4$      | $14 \pm 3$                                   | $42 \pm 9$      |
| CO                         | $4.7 \pm 2.7$                                | $7.4 \pm 3.7$   | $8.7 \pm 3.3$                               | $9.4 \pm 2.8$   | $4.5 \pm 2.6$                                | $9.6 \pm 7.9$   |
| $\text{CH}_4$              | $0.3 \pm 0.002$                              | $0.3 \pm 0.004$ | $0.3 \pm 0.001$                             | $0.3 \pm 0.004$ | $0.3 \pm 0.001$                              | $0.3 \pm 0.006$ |
| NMHCs                      | $25 \pm 3$                                   | $26 \pm 3$      | $26 \pm 4$                                  | $30 \pm 2$      | $9.0 \pm 1$                                  | $32 \pm 4$      |
| alkanes                    | $6.9 \pm 0.8$                                | $3.5 \pm 0.5$   | $3.3 \pm 0.9$                               | $3.6 \pm 0.5$   | $1.7 \pm 0.2$                                | $7.5 \pm 1.1$   |
| alkenes                    | $14 \pm 3$                                   | $18 \pm 2$      | $19 \pm 4$                                  | $21 \pm 2$      | $4.9 \pm 0.9$                                | $15 \pm 3$      |
| ethyne                     | $0.1 \pm 0.1$                                | $0.2 \pm 0.3$   | $0.1 \pm 0.1$                               | $0.2 \pm 0.1$   | $0.1 \pm 0.1$                                | $0.2 \pm 0.2$   |
| aromatics                  | $4.0 \pm 0.6$                                | $4.7 \pm 0.7$   | $3.2 \pm 1.0$                               | $5.5 \pm 0.8$   | $2.3 \pm 0.2$                                | $8.9 \pm 2.3$   |

**Fig. 10** **a** Average OH reactivity and **b** percentage contribution of CO, CH<sub>4</sub>, and different classes of NMHCs calculated for Jeddah, Mecca, Madina, Lahore, and Singapore



calculated for Singapore ( $4.8 \pm 0.2 \text{ s}^{-1}$ ), about twice that obtained for the Saudi Arabia background ( $2.7 \pm 0.1 \text{ s}^{-1}$ ), and a very high  $k_{OH}$  value for Lahore ( $117 \pm 7 \text{ s}^{-1}$ ). The percentage contribution of the different classes of NMHCs to  $k_{OH}$  is overall consistent across the different urban areas (Fig. 10b) although methane's contribution to  $k_{OH}$  was relatively high in Singapore (6 %) because of the relatively smaller contributions from CO and the NMHCs. In addition, isoprene (mostly from vegetation) was the largest contributor to  $k_{OH}$  among the alkenes in Singapore.

## 5 Final remarks and conclusions

The ground-based samples collected in October–November 2012 and April 2013 in Jeddah, Mecca, and Madina were analyzed for CO, CH<sub>4</sub>, and a large suite of NMHCs and compared to the local background and to samples collected around the same period in Lahore and Singapore. The most abundant NMHCs in Saudi Arabia were the C<sub>2</sub>–C<sub>4</sub> alkanes, pentanes, ethyne, ethene, propene and toluene. The highest NMHC load was measured in Jeddah ( $99.6 \pm 9.6 \text{ ppbv}$ ) followed by Mecca ( $79.5 \pm 8.4 \text{ ppbv}$ ) and Madina ( $52.8 \pm 10.6 \text{ ppbv}$ ) where many NMHCs were found significantly higher during the nighttime compared to daytime. In comparison, a remarkably higher load was observed in the Lahore samples ( $407 \pm 29 \text{ ppbv}$ ). Despite the differences in the absolute mixing ratios, when the general patterns in NMHCs were analyzed, similarities were

observed among these different urban centers, particularly for the aromatic fraction, suggesting that the composition was mainly driven by the same sources. Compared to US cities (Baker et al. 2008) and Karachi (Barletta et al. 2002), the median value for many NMHCs measured in the Saudi Arabian and Pakistani cities was higher than the mean value reported for any of the 28 US cities. In Mecca, Madina and Lahore the contribution to the total NMHCs from the combustion product ethyne was particularly high compared to the other cities; while the ethane composition in all Saudi Arabian cities was particularly low (4–5 %) compared to the other centers. A high contribution was observed from the pentanes (19–25 %) in Saudi Arabia, and propane and butane were particularly important in Jeddah (35 % of total NMHCs).

A comparison with the MACCity global chemistry emissions inventory revealed some discrepancies in the relative contribution of several NMHCs (or groups of NMHCs) between the measurements and the data inventory. In particular, the Saudi Arabian city measurements showed that the inventory underrepresented fast reactive alkenes, which could have significant implications when such inventories are used in chemistry models for forecasts and hindcast analyses of ozone and tropospheric composition.

Bearing in mind the limited sampling size available for each city, a significant source (or sources) of short chain alkanes (propane and butanes) was observed in Jeddah. However, we were not able to identify the nature of this specific source(s). LPG leakage is ruled out because of the lack of cross correlation among these gases, and combustion is ruled out because of the lack of correlation with the combustion tracer CO. In Madina, vehicular emission was the predominant NMHC source; while a combustion source in combination with fuel evaporation has a strong impact on many of the NMHCs measured in the urban area of Mecca. Leakage from natural gas is suggested to be the main source of the remarkably high levels of methane measured in Lahore.

Carbon monoxide, alkenes and aromatics play the most important role in terms of  $k_{\text{OH}}$ , while the alkanes were minor contributors. Overall, the  $k_{\text{OH}}$  derived for the Saudi Arabian cities falls within the range reported for other urban centers worldwide; while Singapore and Lahore represent two opposite extremes.

We remind how different urban areas are affected by different factors such as meteorology, specific dynamic urban flow and other elements which all affect the measured mixing ratios. While we were not able to quantify such factors (but they are worthwhile to be considered in future works), our study is a first step in building a database for Saudi Arabian NMHC emissions and two other Asian cities and further shows the importance of different classes of NMHCs, and individual species, to OH reactivity.

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